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Superlattice effects on the amorphization of Ni-Ti multilayers

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ABSTRACT

A phenomenological model is proposed to correlate the onset of solid-state amorphization with the loss of interfacial stability in Ni-Ti multilayers. Additionally, a temperature dependence to the onset of amorphization is attributed to the effect of interfacial coherency that varies with the Ni-Ti layer pair spacing.

INTRODUCTION

Solid-state amorphization (SSA) is the growth of a disordered phase as a result of mixing two or more crystalline phases. Long-range order in the amorphous phase is less than the crystalline phase. Not all material systems will undergo SSA but when it does occur, the reaction can be induced thermally. The phenomena of the SSA process can be examined by preparing metallic multilayer films. The crystalline phases interdiffuse at layer interfaces forming the amorphous phase. Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) can be used to monitor heat flow indicating the change in state of crystallinity. The SSA and recrystallization processes in multilayer films is often associated with a broad exothermic peak in DSC measurements.[1-3] Although the exotherm of the diffusion process is indicative of growth, homogenization and recrystallization of the amorphous phase, it may not indicate the nucleation of the amorphous phase.

In the deposition of metallic multilayer films, it is widely known that the process parameters influence the energetics of the growing film.[4] For the case of Ni-Ti multilayers, sputter deposition conditions exist for an epitaxial growth. In-situ observations using transmission electron microscopy confirm that the as-deposited, crystalline multilayer structures are temperature sensitive.[5] Upon heating the multilayer films, a SSA reaction is found to occur nucleating at the Ni-Ti interfaces. This result is expected as amorphization can originate at interface sites of both composition and crystalline disorder. A temperature dependence to the onset of the SSA is measureable using DTA.[6] SSA occurs at progressively higher temperatures in Ni-Ti multilayers as the layer period decreases. X-ray diffraction characterization indicates that lattice strains in the Ni and Ti layers vary with the multilayer spacing.[7] The multilayer looses coherency as the layer pair spacing increases from very short periods. A phenomenological model is now proposed that correlates the loosing the energetic barrier to amorphization in crystalline multilayers with the loss of (interfacial) lattice stability.

MODELING

A criteria is proposed for nucleating an amorphous phase in a multilayer by crystalline phase intermixing. The nucleation event for SSA may be indicated by a critical temperature coinciding with a discrete endotherm and loss of crystallinity. This differs from subsequent heat flow from the ensuing reaction between the crystalline and amorphous states as routinely associated with a broad exotherm. The proposed model correlates experimental results for the Ni-Ti multilayer system with the nucleation event to SSA.

The free energy levels for the stable and metastable crystalline phases as well as the amorphous phase are illustrated (Fig. 1) with the corresponding activation energies of each

transition. The free energy versus activation energy plot is adapted for the case of crystalline multilayers from a phenomenological model of crystal to amorphous phase change developed by Brazhkin.[8] The free energy for the stable and metastable crystalline phases are defined as F(x) and $F(m_i)$, respectively, where 'i' is the number of atomic planes within each layer. The free energy is F(a) for the amorphous phase. It's assumed that the free energy F(x) is less than $F(m_i)$ which is less than F(a). The multilayer structure is a metastable crystalline phase and the starting point for the SSA analysis. The multilayer structure is artificial and assumed to be intrinsically metastable. For the case of crystalline layers in a superlattice structure, it's assumed that the free energy is dependent upon lattice distortions within each layer. The lattice distortions are related to the disorder at the interfaces and within each layer. The activation energy for the transition from the multilayer crystalline phase to the stable crystalline phase is defined as $\Delta G(m_i x)$. A stable crystalline phase is an equilibrium phase as, for example, a solid solution or intermetallic. The activation energy for the transition from the multilayer crystalline phase to the amorphous phase is defined as $\Delta G(m_i a)$. It is assumed that in order for SSA to occur, $\Delta G(m_i a)$ must be less than $\Delta G(m_i x)$.

Let's consider the following scenarios for SSA in a multilayer composed of two chemically unique and crystalline components. The shortest layer pair spacing is that of alternating monolayers. The number of atomic planes for each constituent equals 1 within a layer. The i = 1 case for crystalline multilayer structure is a single phase and artificially coherent superlattice with a corresponding free energy of $F(m_1)$. It is assumed that the activation energy $\Delta G(m_1 x)$ is less than $\Delta G(m_1 a)$ inferring that the multilayer will not undergo SSA. An increase in the number of atomic planes per layer pair in the as-deposited multilayer can produce an increase in superlattice distortion, hence an increase in the disorder and the free energy of the multilayer. The local perturbation in both long and short range order seeds the

transformation to the glassy phase. Therefore, the onset of SSA is possible once a critical number i(c) of atomic planes is exceeded in the layer pair, i.e. $i > i(c)$. SSA occurs when disorder in the multilayer increases with the number of atomic planes to a state where $\Delta G(m_i x)$ is greater than $\Delta G(m_i a)$.

EXPERIMENTS AND RESULTS

Sample preparation

The specimens of this study are prepared by planar magnetron, sputter deposition. A 3nm thick buffer layer of Ni is first deposited onto Si and cleaved mica substrates. The buffer layer is the template to initiate an epitaxial growth of the multilayer. The deposition parameters of low working-gas pressure (<1 Pa), low discharge voltage (<250 V) and a long source-to-substrate separation (>10 cm) provide a condition for near thermalization of the sputtered neutrals. These process parameters minimize the effects of energetic sputtered neutrals, that is ballistic adatom bombardment at the substrate. Intermixing is minimal and amorphization is eliminated at the interfaces in the as-deposited state thereby providing a continuous crystalline growth for the multilayer superlattice.[9] The superlattices are deposited to span a composition range from 13 to 42 at.% Ni. The composition of the multilayers is analytically verified using Auger electron spectroscopy coupled with depth profiling.[9] The measured composition of the Ni-Ti multilayers is referred to in ensuing sample characterization.

Structural characterization

Transmission electron microscopy (TEM) of the multilayer samples prepared in cross-section reveals the growth morphology as well as providing a measure which confirms the

thicknesses of the Ni and Ti layers. The layering is smooth and continuous normal to the growth direction with compositionally abrupt interfaces.[5,10] High resolution TEM of the cross-sectioned multilayers reveals both the Ni-Ti and Ti-Ni interfaces to be crystalline.[9-11]

X-ray diffraction provides a measure of the layer pair spacings, the composition profile along the growth direction, and lattice distortions. Analysis of Cu $K\alpha$ diffraction scans in the $\theta/2\theta$ mode taken at glancing (0°-12°) angle reveals a (near) square-wave composition profile along the growth direction.[7] Intermixing at the interfaces is computed to be only one to two atomic planes for the Ni-Ti multilayer samples. Analysis of diffraction scans taken at high (30°-60°) angle using dynamical diffraction theory indicates the lattice spacing variations along the [111] of the composition modulation are attributed to strained layers.[7] The Ni layers are computed to be in tension whereas the Ti layers are in compression. For example, the lattice spacing and computed strain variation are plotted (Fig. 2) along the direction of composition modulation for a 8.2nm layer pair where $i_{Ni} = 16$.[7] The atomic planes in the Ni-Ti superlattices are all lattice strained for layer pair spacings less than 10-12 nm, whereas above 10-12 nm the lattice strain relaxes from a maximum at the interfaces to a zero at the center of each layer.

Amorphization measurements

The Ni-Ti multilayer samples are prepared and tested for SSA.[6] The Ni-Ti multilayer foils are floated from the mica substrates using a deionized water bath. The air dried foils are cut to 1.5-2.5 mg sample weights. The samples are placed in the DTA, heated to 200 °C at a rate of 20 °C min^{-1}, and then slowly heated to 430 °C at a rate of 0.5 °C min^{-1}. The DTA output is a thermal trace that plots the difference in temperature (ΔT) between an alumina powder standard and the Ni-Ti multilayer as a function of increasing temperature (T). The DTA scans for the Ni-Ti multilayers indicate an *endothermic* reaction for the nucleation event of SSA.[6]

The amorphization temperature (T_a) is indicated by a discontinuous decrease of ΔT with temperature at $T = T_a$, that is, where $\partial^2(\Delta T)/\partial(T)^2 < 0$. As an example, the $\Delta T(T)$ trace (Fig. 3) for a 26nm layer pair film where $i_{Ni} = 31$ indicates SSA occurs at 307°C. A summary plot (Fig. 4) of the results for groups of Ni-Ti multilayer samples indicate that a minimum value in $T_a(i)$ is reached for $i_{Ni} > 25$. The minimum value coincides with full relaxation of the superlattice.

ANALYSIS AND DISCUSSION

Analysis of the diffraction data indicates the lose of coherency for $i_{Ni} > 3$ multilayers. It corresponds that SSA is only observed for $i_{Ni} > i(c) = 3$, as $\Delta G(m_3a) < \Delta G(m_3x)$. The disorder increases with layer pair spacing to a condition where the superlattice strain is *fully relaxed* for cases where $i_{Ni} > 25$.[7] If an assumption is made that the energetic barrier to amorphization is proportional to the square of the lattice strain ($\varepsilon_{[111]}^2$), then an assessment of the strain effect on T_a is tractable. To a first approximation, the strain-energy barrier (ΔG_ε) can be computed as a summation of $\varepsilon_{[111]}^2$ for each atomic plane (n) of Ni within the layer pair normalized to the number of Ni atomic planes (i_{Ni}). That is,

$$\Delta G(i)_\varepsilon = \sum_{n=1}^{i} \{\varepsilon(n)_{[111]}^2\}(i_{Ni})^{-1} \qquad (1)$$

For a $i_{Ni} = 16$ case, i.e. the 8.2 nm multilayer of Fig. 2, the value of $\Delta G(16)_\varepsilon = 0.0026$ is computed from eqn. (1) using the lattice strain values as determined by dynamical x-ray diffraction modeling.[7] Similarly, for a $i_{Ni} = 3$ case, $\Delta G(3)_\varepsilon = 0.0050$ whereas for a $i_{Ni} = 25$ case, $\Delta G(25)_\varepsilon = 0.0016$. The result that $\Delta G(3)_\varepsilon > \Delta G(16)_\varepsilon > \Delta G(25)_\varepsilon$ thus corresponds with the progressive decrease in T_a. The increase in the layer pair spacing coincident with $1 < i_{Ni} < 25$

corresponds to an increase in free energy, where $F(m_{25}) > F(m_i) > F(m_1)$. The activation energy for SSA decreases, e.g. $\Delta G(m_{25}a) < \Delta G(m_{16}a) < \Delta G(m_3a)$, with a progressive increase in layer pair spacing and disorder. A progressive decrease in the nucleation temperature (T_a) of SSA is measured as the layer pair spacing increases coincident with an increase of i_{Ni} from 3 to 25.

Observation of the nucleation event to SSA provides additional information to the heat flow measurements for multilayers that exhibit broad exotherms for mixing of the amorphous and crystalline phases, homogenization and (subsequent) intermetallic formation. Recrystallization occurs subsequent to homogenization, i.e. once the instability to the (compositionally-induced) short range disorder has vanished. The absence of an endotherm for SSA nucleation in some heat flow measurements can be linked to the interface structure of the as-deposited multilayer. An amorphous interfacial structure rather than a crystalline superlattice can be formed in as-deposited Ni-Ti multilayers as a consequence of an energetic sputter deposition process.[9] If an amorphous interface phase is present in the as-deposited structure, then only the ensuing broad exotherm is found using calorimetry.[1-3]

SUMMARY

It is observed that the nucleation of an amorphous phase in Ni-Ti multilayer superlattices occurs at the site of crystalline (long-range) disorder. Long-range disorder alone is not a sufficient criteria for SSA. Amorphization from an instability that exists from compositional (short-range) disorder, for example, as driven by thermally induced interdiffusion. SSA can occur at either crystalline-amorphous or crystalline-crystalline interfaces. The later case is the subject of the proposed model for the following phenomena. An additional energetic barrier to SSA can be present in the form of superlattice strain. This

constraint appears to raise the temperature needed for SSA. Once an amorphous phase forms at the crystalline interfaces, it grows at the expense of the crystalline phase. In any case, the activation energy to transform a metastable crystalline phase to an amorphous phase is less than that for recrystallization. Once the amorphous phase is homogenized restoring short-range order, the *instability* for the glassy phase is lost, and subsequent recrystallization coincides with the return of long-range order.

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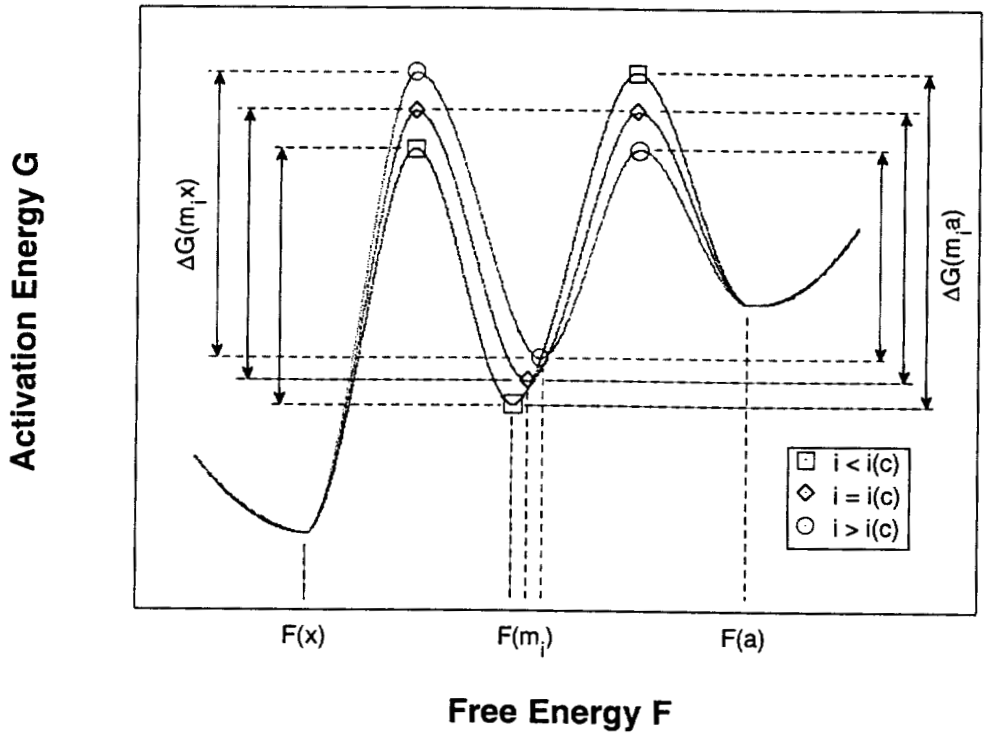

Fig. 1 The levels of free energy F(x), $F(m_i)$ and F(a) are illustrated for the stable crystalline, metastable crystalline and amorphous phases, correspondingly. Activation energies are shown for the metastable multilayer to stable crystalline transition $\Delta G(m_i x)$, and the metastable multilayer to amorphous phase transition $\Delta G(m_i a)$.

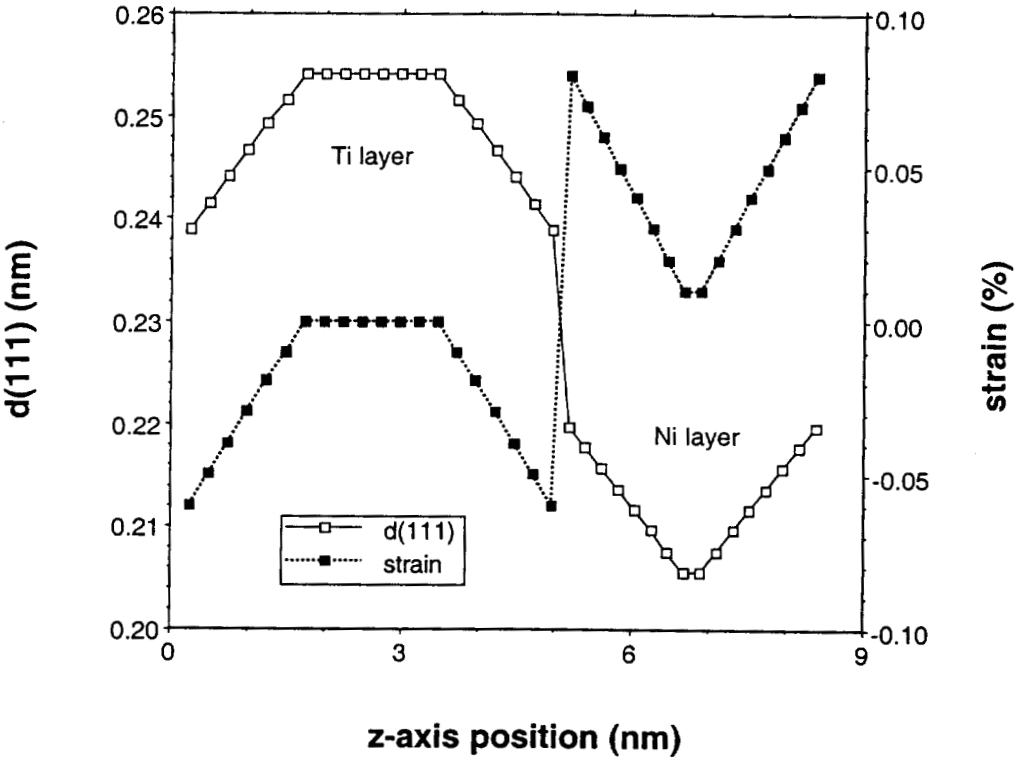

Fig. 2 The lattice spacing d (nm) and computed strain (ε) along the [111] modulation direction are plotted for a 8.2 nm layer pair, Ni-Ti superlattice film.

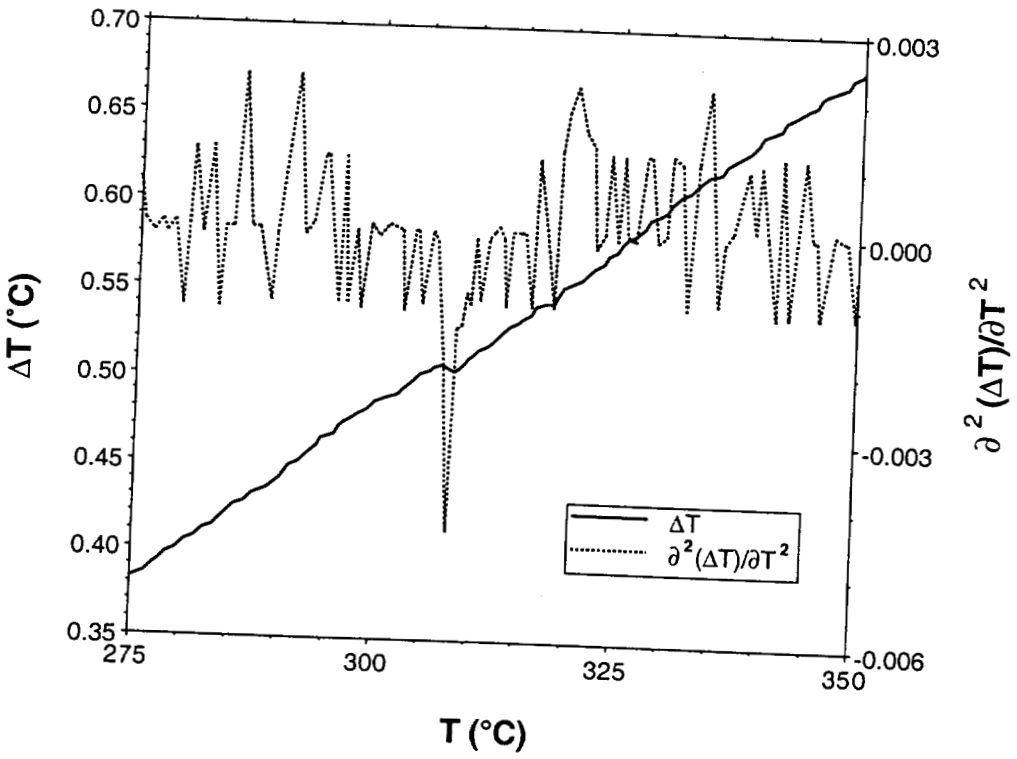

Fig. 3 The temperature T (°C) for solid-state amorphization (T_a) coincides with a decrease in the change in temperature ΔT (°C), i.e. when $\partial^2(\Delta T)/\partial(T)^2 < 0$, for this differential thermal analysis trace of a 26 nm layer pair, Ni-Ti superlattice.

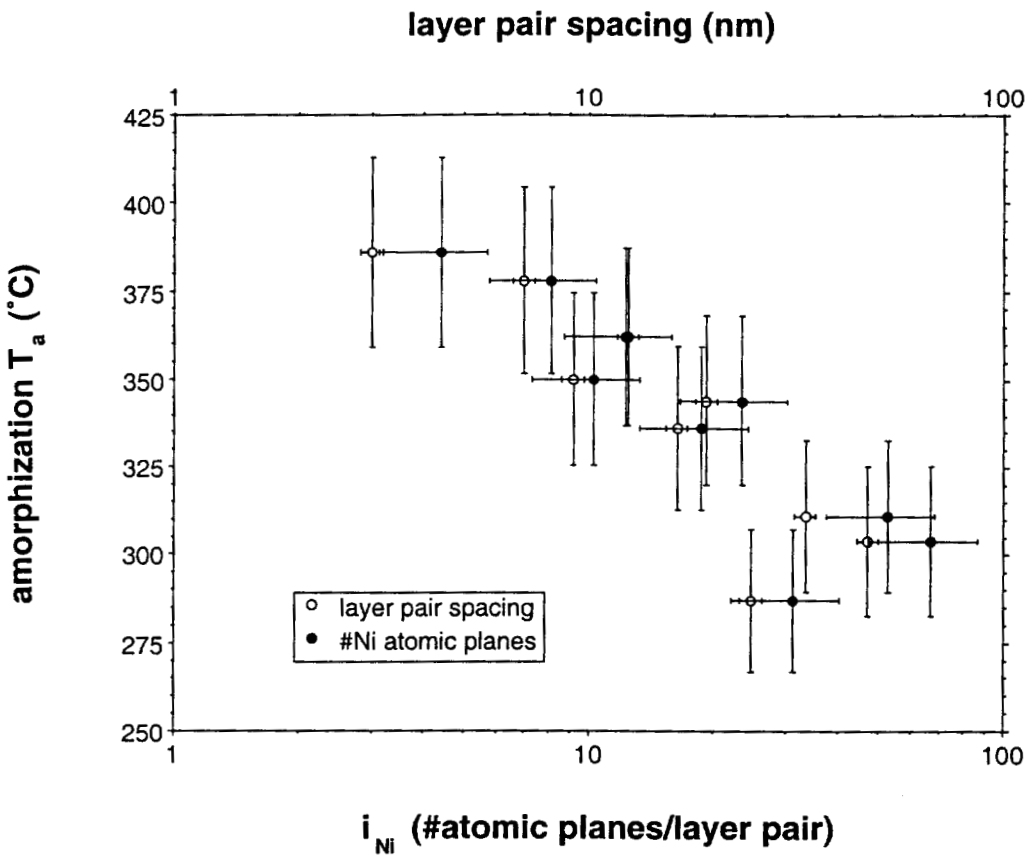

Fig. 4 The temperature for solid-state amorphization T_a (°C) varies with the number of Ni atomic planes (i_{Ni}) and the layer pair spacing (nm) for Ni-Ti multilayer superlattices.